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The Effect of Composition of Roman Cement Repair Mortars on Their Salt Crystallization Resistance and Adhesion

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Abstract

Crystallization of soluble salts in porous networks is a major source of decay for mortars used in historical buildings. The optimum formulation and application of Roman cement mortars which could produce compatible and durable repairs of the original substrates was studied. Measurements were performed with the aim of determining the pore size distribution, the hydric parameters as well as the salt crystallization resistance of the mortars. The adhesive strength of the repair materials laid on historic substrates was also determined. The results of the crystallization tests show that repair Roman cement mortars with hydric parameters close to those of the historic substrates, though different pore size distributions, have related salt crystallization resistance.

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Keywords: Roman cement, historic mortars, pore structure, salt crystallisation, adhesion, mercury porosimetry.

1. Introduction

Highly hydraulic binders, known as natural or Roman cements, were key materials for the economic and easy manufacture of renders and cast architectural details for the exteriors of buildings during the nineteenth and early twentieth century [1]. The growing availability of Roman cements for the conservation field has raised important questions about the compatibility between historic and repair mortars. Compatibility is broadly defined as the capacity of the repair mortar to interact with the original historic material without causing any damage, directly or indirectly [2]. Application of an old recipe or mimicking of properties of original mortar gives no guarantee of material compatibility because both materials evolve in course of time. As the properties of the repair mortars can vary due to the interaction of fresh mortars with the substrate during hardening, several combinations of historic substrates and repair mortars should be studied.

Crystallization of soluble salts in porous networks is a major source of decay for mortars used in historical buildings. The principle of this decay is roughly explained as salts crystallizing in the porous networks and causing stress inside the pores [3], [4]. This stress is responsible for the internal cracking of the mortar. The type of damage depends on the type of salt as well as on the characteristics of the materials. The mortars and stones that are most sensitive to salt decay are generally those with high porosity and high rate of water evaporation. The decay of natural stones caused by salt crystallization has been widely discussed [5–7]. However, in the context of porous building materials, the crystallization of soluble salts in Roman cement mortars has never been described.

One of the principal aims of this study was to identify scientifically-sound criteria for the optimum formulation and application of Roman cement mortars that could produce compatible and durable repairs of the original substrates. Good adhesion between the original and the repair material is another vital condition necessary for the proper execution of conservation work. Otherwise, any factor reducing the adhesive strength of the repair can make a good repair material

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incompatible. Only a few publications report on the adhesion strength between repair material and concrete substrate [8], [9]. The pore structure of the mortars is one of the main properties responsible for their compatibility as it greatly influences water adsorption, shrinkage cracking [10] and strength. The mismatch in the pore structure at the substrate-mortar interface may lead to a zone of damage due to salt crystallization affecting the adhesive strength of a repair, and thus compromising its final compatibility. Repair mortars should be less durable than the historic substrate; their role should ultimately be sacrificial. Different wetting and drying rates may also adversely affect the appearance of the repair, whereas a repair mortar with too high strength imposes stress on weaker masonry or stuccoes.

This paper describes the influence of mortar composition on their salt crystallization resistance. Mortars with different composition may enhance water and salt solution transport resulting in different types of damage. To establish the compatibility of historic and repair mortars, salt crystallization resistance tests were performed on sandwich samples composed of different substrates covered with historic and repair Roman cement mortars. Sodium sulphate was the agent selected for this study since it is widely known as the most destructing salt affecting porous building materials and its damaging mechanisms are well known [11–13]. Measurements of the adhesive strength of repair materials laid on historic substrates were also performed while good adhesion of repair mortars was another criterion for the compatibility assessment. In the case of poor adhesion, local delamination between the mortar and the substrate layer may occur resulting in crystallization of salt in areas without strict adherence.

2. Materials and methods

The formulation of the restoration mortars used in this study replicated some representative groups of historic mortars. Two sets of repair mortars were prepared from Folwark Roman cement (Poland) by mixing the cement with the aggregate (a/c = 0.5 by weight). Quartz sand (d = 0.25–0.5 mm) was used as the aggregate. The mortars were produced at water-to-cement ratios varying from 0.6 to 1.0. Due to the quick setting of the cement, citric acid was added as a retarder at 0.3 wt.% (relative to dry cement). Mortars were casted into silicone molds. Masonry samples with two different types of joints were considered. The first set consisted of newly prepared mortars specimens of 5×5×2 cm. The second set of specimens consisted of a fired-clay brick substrate or historic substrates (Imperial Palace Hofburg, Vienna, Austria; core of a casting) with laid Roman cement repair mortars. During preparation of the sandwich samples, the substrates were pre-wetted by soaking in water. Specimens were about 5×5×5 cm^3 with the plaster layer being approximately 2 cm thick. The materials were then de-molded after setting and stored in humid air at 100% relative humidity (RH) conditions for 3 months to ensure wet curing conditions. The influence of different curing conditions on hydration has been previously described [14]. The lack of moisture in the external conditions may result in incomplete hydration and affect the microstructure and strength of the mortars. In real world conditions, ideal wet-air curing of mortars is rarely possible in the course of practical work on the façade. The characteristics of the original marl feedstock, the calcinations conditions, the oxide and mineralogical compositions of the cements, as well as their strength and porosity development in the progress of hydration have already been reported [15].

The pore structure of the mortar samples was determined using a Poremaster mercury intrusion porosimeter (quantachrome), which allows studying pore sizes in the range of 440–0.0035 μm. After the predetermined curing period, the specimens were immediately soaked in acetone for 24 h to stop the hydration of the cementitious materials [16], [17]. Afterwards, they were placed in a rotary vacuum evaporator flask at 20 °C for 4 h to remove the acetone and were finally allowed to dry.

Salt crystallization cycling allows determining the resistance of mortars to salt attack. Salt crystallization cycles were performed according to the procedure given by ASTM C88-05 [18]. Mortar/brick and mortar/historic substrate specimens of 100 ± 20 g were used for testing. Prior to each cycle, specimens were weighed. The samples were immersed in a 14% sodium sulphate decahydrate ($Na_2SO_4 \cdot 10H_2O$) solution for 4 h. The density of this solution at 20 °C is 1055 kg/m^3. They were then removed from the solution and left to dry in an drier at 60 °C for 8 h and later left to cool to room temperature for 6 h. Their individual masses were noted before continuing the soaking in the salt solution. Sample cubes were subjected to 15 cycles except in the event of failure or disintegration of the cubes occurring before completion.

Hydric tests including the determination of the free water absorption (A_F), the saturation coefficient (S) and the water absorption by capillarity (C) were performed to characterise the parameters associated with fluid uptake and transport inside the pores according to the procedure recommended by PN-EN 1015-18 [19]. The calculations were performed using the procedure described previously [20].

The adhesion of repair mortars has been studied on composite samples, which were prepared by applying a repair mortar onto historic Roman cement substrates and bricks. Pull-off strength measurements are recommended for the assessment of the adhesive strength between concrete substrates and repair materials. The pull-off test was carried out with a digital apparatus PosiTest pull-off adhesion tester. Steel disks of 50 mm in diameter were bonded to the top of each repair mortar with epoxy glue. Pull-off tests were performed according to the procedure recommended by ASTM D7234–12 [21].

3. Results and discussion

Porosity and pore size distribution are important parameters used for describing a hydrated cement system when the physico-chemical behaviour and the durability of repair mortars is considered. Figs. 1 and 2 compare the differential volume of intruded mercury as a function of pore diameter for the Roman cement mortars prepared using water-to-cement ratios (w/c) of 0.6 and 1.0, studied after aging for 1 day and 3 months, respectively.

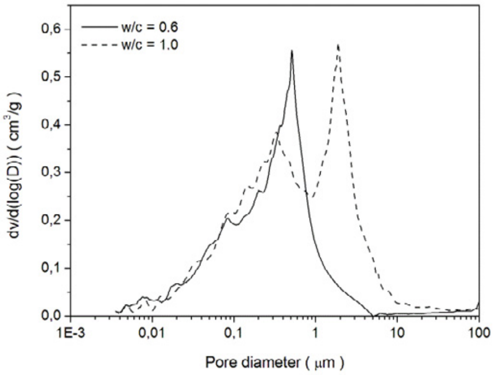

Fig. 1. Differential volume of intruded mercury vs pore diameter for mortars with w/c ratio of 0.6 and 1.0 cured for 1 day

These repair mortars were prepared using typical historic mortar formulations, which were previously studied by the authors [22]. The mortars with less amount of water represent the typical formulation of the cast mortars while the latter with 1.0 w/c is rather close to the rendering mortar. A curing time of 1 day represents fresh or low hydrated mortars; 3 months of hydration at ideal moist curing conditions is considered sufficient for complete hydration.

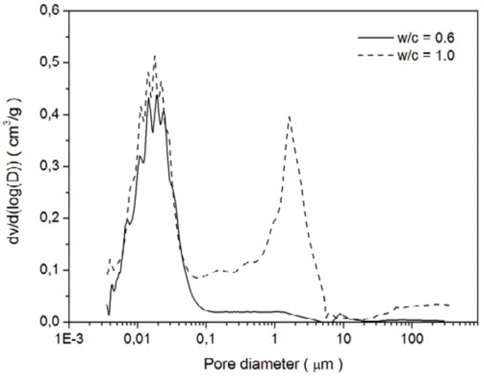

Fig. 2. Differential volume of intruded mercury vs pore diameter for mortars with w/c ratio of 0.6 and 1.0 cured for 3 months

After studying the porous structure of Roman cement repair mortars, the unimodal peak at 0.7 µm was observed for the 1-day old specimen prepared at the w/c ratio of 0.6. With the increase in water content, the bimodal pore structure can be observed. The initial peak shifts to higher pore diameters with a maximum at 1.9 µm. The second porosity region, similar as the one found in 0.6 w/c mortars, can be noticed with a pore diameter of 0.3 µm. For samples cured for 3 months, the threshold pore diameters are reduced to 0.01–0.03 µm. This shift is the result of the progress of hydration and the closing of the broad pore diameters by the growth of the C-S-H gel. However, the mercury intrusion curves point to the presence of larger pores of 1.20 μm in diameter for samples prepared at w/c ratios of 1.0. This observation can be interpreted in terms of an insufficient amount of C-S-H gel required to fill the large pores present in the structure due to an excess amount of water.

Similar pore-size regions were observed in historic Roman cement mortars with pore diameter values that were dependent on the initial water to cement ratio (w/c) or curing conditions. The finest pores, with diameters below 0.2 μm, were present within the hardened aged Roman cement matrix. Pore diameters shift to smaller values in the case of well-hydrated and matured Roman cement mortars, which were exposed to wet-curing conditions over a long period of time (e.g. stucco, cast ornaments).

Larger 'air' pores, with diameters between 0.2–2 μm, are due to the evaporation of excess unbound water and restricted hydration. They were characteristic of materials in which the hydration process was interrupted by the evaporation of water. Pores larger than 2 μm were induced by shrinkage drying and mortar weathering [22].

The porous structure of fired-clay brick has a very close pore size distribution relative to that of historic Roman cement mortar. The only difference lies in the region of macropores whose maximum is shifted to 3.0 μm showing a sharp peak with very narrow distribution (Fig. 3).

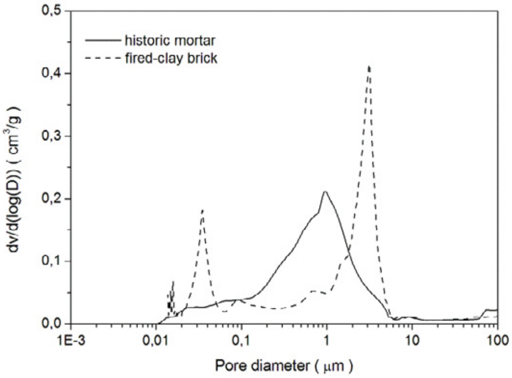

Fig. 3. Differential volume of intruded mercury vs pore diameter for a Roman cement historic mortar and a fired-clay brick

The weathering processes greatly depends on the porous structure and the water circulation inside the materials. A comparison of pore and hydric parameters of brick, historic and repair Roman cement mortars after 3 months of hydration is shown in Table 1. These results are complemented by the water absorption curves, which show the water behavior due to capillary action of the repair mortars and both substrates (Fig. 4).

Table 1. Porosity and hydric parameters of historic substrates and Roman cement repair mortars hydrated for 3 months.

Sample	Total open porosity [%]	Pore diameter [μm]	Free water absorption, A_F [%wt]	Saturation coefficient, S [% v/v]
Roman cement repair mortar w/c = 0.6	30	0.01–0.03	22	42
Roman cement repair mortar w/c = 1.0	52	0.01–0.03 1.20	27	45
Roman cement historic substrate	22	0.03–0.1 1.0	20	36
Fired-clay brick substrate	23	0.02–0.04 3.0	17	29

The hydric parameters obtained for the Roman cement repair mortar with w/c ratio of 0.6 are only slightly higher from the ones obtained for the Roman cement historic substrate. The repair mortars prepared with higher w/c ratio possess more open spaces inside the matrix. This results in higher free water absorption compared to the repair mortars with lower w/c ratio as well as to that of obtained for the two original substrates. The water absorption by capillarity shows considerable water uptake of both repair mortars. This is mainly due to their high percentage of very small pores and their total porosity values.

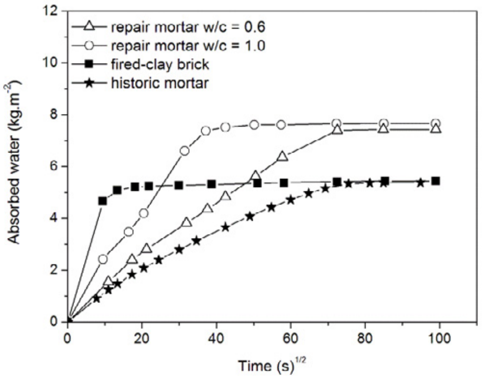

Fig. 4. Water absorption by capillarity for a fired-clay brick, a historic mortar substrate and a Roman cement repair mortar with w/c ratio of 0.6 and 1.0, cured for 3 months

The fired-clay brick and historic Roman cement substrate has lower water absorption by capillarity due to the lower total porosity that can be filled by water. Another general observation can be made from water absorption measurements – both repair Roman cement mortars and both substrates show fast transport of the water to the surface which determines the condition for crystallization of the salts on the surface of the materials. The small differences in the water absorption rate between the materials can be similarly related to the amount of capillary pores, which are active in water transport. It can be observed that the smaller the pores, the greater the capillary absorption.

The results of salt crystallization resistance of Roman cement repair mortars with varying w/c ratios for a fired-clay brick and a historic mortar substrate during 15 cycles of artificial aging in saturated sulphate solution are presented in Fig. 5. Analysis concerning the resistance to sulphates revealed that Roman cement repair mortars with w/c ratio of 1.0 collapse prematurely, with total destruction at the 8 cycle. In contrast, for the repair mortars with w/c ratio of 0.6, the deterioration occurred at a much slower rate. For repair mortars with lower w/c ratio, the first signs of damage were visible at 8 cycles and total destruction was noted at the 14 cycle similar to that obtained for the Roman cement historic substrate.

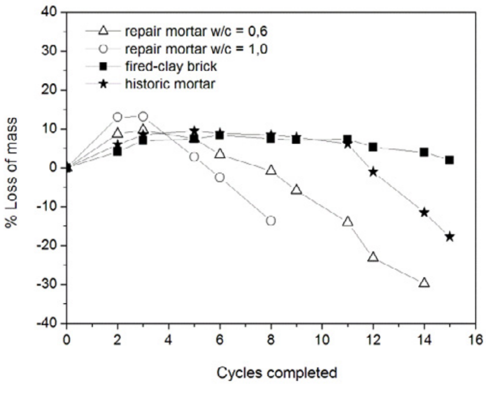

Fig. 5. Loss of mass (%) in relation to the initial mass of Roman cement repair mortars with w/c ratio of 0.6 and 1.0 cured for 3 months, a fired-clay brick and a historic mortar substrate during 15 cycles of artificial aging in saturated sulphate solution

For a porous materials such as stone, particular attention has been placed on the relationship between pore radius distribution and the resistance of the material to mechanical damage caused by salt crystallization. According to Angeli *et al.* [23], crystal growth of salts is favored in large pores because the chemical potential of crystallites depends inversely on their radii. This is due to the contribution of crystal surface energy, which increases when the crystal size decreases. Crystal growth in the smaller pores can start only after the larger pores are completely filled. At this moment, the increasing pressure of the crystals on the pore walls renders the chemical potential of the crystals equal in both classes of pores. According to Lanas *et al.* [24] and Cavdar and Yetgin [25], salt crystallization and mechanical stress are the most effective causes of degradation of lime-based mortars used in renders. Decay due to salt attack is most noticeable in mortars with high porosity and low strength. In the case of Roman cement repair mortars, a similar situation can be noted. For Roman cement repair mortars with bimodal pore size distribution, the salt crystallization resistance is less compared to mortars with unimodal pore size distribution. Also, the higher amount of absorbed water and salt solution, as shown in previous experiments, can contribute to a more pronounced degradation pathway of the repair mortars.

Most crystallization tests reported in the literature are meant to assess the resistance/durability of certain materials to salt crystallization. Accordingly, they are performed on specimens made of a single material (concrete, mortar, brick, stone, etc.). Plasters and renders do not work independently of the substrate. Therefore, in the case of incompatibility of these two materials, their detachment is already evidence of damage, even if no other deterioration occurs in the plaster/render or in the substrate materials. The strength of adhesion profiles of repair mortars with w/c ratio of 0.6 and 1.0 cured for 3 months laid on a water-soaked brick and a Roman cement historic substrate is shown in Fig. 6.

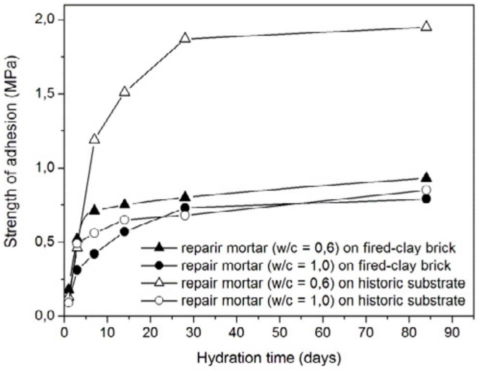

Fig. 6. Adhesion of repair mortars with w/c ratio 0.6 and 1.0 cured for 3 months laid on a water-soaked brick and a Roman cement historic substrate

A clear correlation between adhesion and curing time, equivalent to the degree of hydration, is observed. The adhesion increases significantly during the first 14 days of hydration when a pull-off strength level of 1.3 MPa is attained for the moist-cured specimen. The parameter further increases during the following 3 months, attaining approximately 2.0 MPa for the sample with a w/c ratio of 0.6 laid on the historic Roman cement substrate. The influence of mortars composition on the pull-off strength values can be clearly seen. Increasing the w/c ratio in the repair mortars lowers their adhesion. Mortars with w/c ratio of 1.0 exhibit comparatively lower values. However, the profiles of the pull-off strength development are the same for both mortars composition. For samples laid on fired-clay brick, independent of repair mortars composition, the strength of adhesion is very similar and also close to the values obtained for repair mortars with a w/c ratio of 1.0 laid on a historic substrate. The results show that mortars with higher porosity and water uptake are more favoured and cause harmful decay. In particular, layer detachment can cause a lack of adhesion between the mortar surface and the brick or the historic substrate.

4. Conclusions

In general, Roman cement stuccoes are in an excellent state of preservation in spite of their usual exposure to polluted urban environments for more than a century. When restoring these materials, particular attention must be paid to an adequate choice of repair mortars, which are critical to the success of the treatment. Compatibility between new repair mortars and the original components of the masonry is highly desirable. It is widely accepted that the problems introduced by replacement mortars are highly complex. However, when considering their resistance and durability to water and water soluble salt action, porosity structure is a crucial parameter that influences the performance of the repair mortar from the point of view of their composition and properties.

In this study, two types of Roman cement repair materials have been studied relative to their original substrates. The mortars differ in water content, which was found to have an influence on their porosity. In the repair mortars, unimodal distribution of pore sizes was observed for low water to cement ratios. With an increase in the water to cement ratios a development of a bimodal pore structure was noticed.

Even though, they were found to develop pore structures close to those of historic substrates which is very well reflected in transport of water and water salt solutions and their resistance to water soluble salts action. In the case of Roman cement repair mortars, a decay due to salt attack is most noticeable in mortars with high porosity. For Roman cement repair mortars with bimodal pore size distribution, the salt crystallization resistance is less compared to mortars with unimodal pore size distribution. Therefore, the above considerations led to the conclusion that they are in broad terms compatible with historic masonry or stuccoes.

However, the porosity of the repair materials can be controlled by a careful manipulation of the water-to-cement ratio of the mix to better adapt them to the properties of the host material. It is important to stress that the selection of repair mortar composition used for renovation purposes should be carried out for each individual case taking into account the substrate characteristics as this factor influences the performance and quality of renderings.

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